Sound Velocity Measurements of $BaCeO_3$ and $BaCe_{0.85}Y_{0.15}O_{2.925}$ Perovskites and Effect of Oxygen Vacancies on the Elasticity

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Introduction: It is generally accepted that the Earth's lower mantle is dominated by $MgSiO_3$-rich minerals with a perovskite structure. Minor elements (such as Ca, Fe, Al), however, may have significant effects on the stability and properties of this perovskite phase[1]. Point defects, for example, may be present in the Mg-rich perovskites containing ferric Fe and Al, a case that has not been established but may play a key role in the understanding of fundamental mantle processes. In contrast to the silicate perovskite, the defect chemistry of ceramic $A^{2+}B^{4+}O_3$ perovskies have been extensively studied. Trivalent rare-earth elements (M = Y, Yb, Nd, Gd) have been found to substitute tetravalent ions, resulting a doped series $A^{2+}(B^{4+}{}_{1-x}M_x)O_{3-0.5x}$, in which the diminished positive charges is compensated by oxygen vacancies. These materials have been considered to be useful analogs for mantle perovskite[2]. Furthermore, the point defects (cation vacancy) have been demonstrated to have a significant influence on the elastic properties[3]. The primary goal of this study is to explore the effect of oxygen vacancies on the elastic bulk (Ks) and shear (G) modulus in these perovskites.

Methods and Materials: Fully-densed, polycrystalline specimen of $BaCeO_3$ and $Ba(Ce_{0.85}Y_{0.15})O_{2.925}$ perovskites, 2.0 mm diameter and 1.0-1.4 mm length, were studied using ultrasonic interferometry at ambient and high pressures, in conjunction with synchrotron x-ray diffraction. The experiment was performed in a DIA-type cubic anvil apparatus (SAM85) installed at the superwiggler Beamline X17B1 at NSLS in Brookhaven National Laboratory. A dual mode Lithium Niobate transducer (10 degree Y-cut, 30 MHz for S wave and 50 MHz for P wave) mounted at the back of the WC anvil enabled us to collect travel time data for both P and S waves in a single experiment. Cubic boron epoxy cube (6.15 mm edge length) was used as pressure medium. The sample was placed in the center of the boron epoxy cube with NaCl and BN as surrounding materials. A glass buffer rod was inserted into the cell assembly between the WC anvil and the sample with gold foils (2 micron thickness) placed at the interface between sample and buffer rod as well as at the buffer rod and WC anvil interface to enhance the mechanical coupling. Additional x-ray diffraction experiments were carried out at ambient temperature only, with the powder samples loaded in fluid (flourinert) medium and teflon capsule. In all experiments, the sample pressure was determined using Decker pressure scale from the X-ray diffraction data for NaCl.

Results: Compressional and shear wave velocities as well as pressure-volume-temperature data were collected at ambient conditions and at high pressure and temperature up to 9 GPa and 773 K. Preliminary data reduction indicates that static compression experiments and ultrasonic measurements at zero and high pressure yielded similar values of ambient bulk modulus for both $BaCeO_3$ (K_0 = 101-103 GPa) and $BaCe_{0.85}Y_{0.15}O_{2.925}$ (K_0 = 102-106 GPa) perovskite. Effects of oxygen vacancies on bulk and shear moduli [G = 48-49 GPa for $BaCeO_3$ and 46-47 GPa for $BaCe_{0.85}Y_{0.15}O_{2.925}$), however, are small in $BaCe_xY_{1-x}O_{3-0.5x}$ perovskites (x = 0 - 0.15), within uncertainties of the experiments. At ambient temperature and at pressures below 2.5 GPa, both $BaCeO_3$ and $BaCe_{0.85}Y_{0.15}O_{2.925}$ perovsites show small but negative pressure derivatives in the shear-wave travel times, as expected for most polycrystalline materials. At higher pressures, however, the shear-wave travel times in both perovskites increase with increasing pressure, resulting a negative dependence on pressure of the shear modulus between 2.5 and 9 GPa. This behavior is regarded to be highly unusual as the ultrasonic measurements were carried out on the polycrystalline specimen.

Conclusions: Our experimental data show that the effects of oxygen vacancies on the ambiemt bulk and shear moduli are small in $BaCe_xY_{1-x}O_{3-0.5x}$ perovskite. The shear-mode softening in these polycrystalline specimen was observed at ambient temperature up to 9 GPa and is likely to be associated with the phase transition previously observed at 22-18 GPa[4]. More experimental work at higher pressures is needed to clarify such unusual shear-mode acoustic properties.

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